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Invention: STRUCTURAL FOAM COMPOSITE HAVING NANO-PARTICLE REINFORCEMENT AND METHOD OF MAKING THE SAME

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This is a:

- ☐ Provisional Application
- ☐ Regular Utility Application
- ☐ Continuing Application
  - ☒ The contents of the parent are incorporated by reference
- ☒ PCT National Phase Application
- ☐ Design Application
- ☐ Reissue Application
- ☐ Plant Application
- ☐ Substitute Specification
  Sub. Spec Filed ________
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  Sub. Spec. filed ________
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SPECIFICATION

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STRUCTURAL FOAM COMPOSITE HAVING NANO-PARTICLE ~~REINFORCEMENT AND METHOD OF MAKING THE SAME~~

BACKGROUND OF THE INVENTION

Foamed plastics are plastics having reduced apparent densities due to the presence of numerous cells disposed throughout the mass of the polymer. Rigid foams usually produced at greater than about 320 kg/m^3 density are known as structural foams, and are well known in the art. Structural foams are commonly used in various aspects of manufacturing molded articles in which low density polymer materials are desirable. Cellular polymers and plastics are made by a variety of methods having the basic steps of cell initiation, cell growth and cell stabilization. Structural foams having an integral skin cellular core and a high strength to weight ratio are made by several processes, including injection molding and extrusion molding, wherein a particular process is selected based upon product requirements.

Injection molding of structural foams is usually conducted under either low pressure or high pressure conditions. For example, during the injection molding process, a chemical blowing agent is typically introduced to the polymer resin melt in the extrusion barrel of an injection molding machine. The temperature of the extrusion barrel is increased under pressure, after which the pressure is released, injecting the polymer into a mold, permitting the chemical blowing agent to generate gas within the polymer. The expansion of the blowing agent pushes molten polymer material against the walls of the mold such that the material in contact with the walls has a higher density than the material toward the middle of the molded article. This establishes a density gradient wherein the outer surface areas of an injection molded article have a greater density than the core of the part due to more foaming in the

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STRUCTURAL FOAM COMPOSITE HAVING NANO-PARTICLE REINFORCEMENT AND METHOD OF MAKING THE SAME

This patent application claims priority from U.S. Provisional Application No. 60/113,134 filed December 21, 1998.

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Substitute Sheet

AMENDED SHEET

center of the article. Thus, a gradient is established having smaller cells present near the mold surface with increasingly larger cells present toward the center of the article.

The use of blowing agents permits short shooting during the molding process. That is, because the blowing agent increases the volume of the expanding polymer composition, the mold is filled with less resin material than would be required without a blowing agent. Consequently, the density of the molded article may be reduced by about 10% to about 20% over articles molded without an incorporated blowing agent. Use of less polymer resin has the advantage of decreasing the weight of the final molded product.

Initiation of cell formation and promotion of cells of a given size are controlled by nucleation agents included in the polymer composition. The nature of cell-control agents added to the polymer compositions influence the mechanical stability of the foamed structure by changing the physical properties of the plastic phase and by creating discontinuities in the plastic phase which allows the blowing agent to diffuse from the cells to the surrounding material. Typically, the resulting cells provide for a lightweight molded article, but do so at the expense of impact resistance. For example, nucleation agents often promote crystalline structures within the cooled polymer, which reduce impact resistance. Mineral fillers may be added to provide a large number of nucleation sites, but such fillers tend to serve as stress concentrators, promoting crack formation and decreasing the impact resistance of molded articles.

Poor impact resistance of structural foam articles may be improved by the inclusion of glass fibers in the polymer melt during processing. However, glass fibers are generally too large to substantially reinforce the foam cells formed by the bubble structures. Glass fibers are often coated with sizing agents, which may induce

clumping and impair even dispersion of the fibers. In addition, the amount of glass fibers required to achieve reasonable impact resistance of structural foam increases the specific gravity of polymer used therein, thereby increasing the density of the foamed article. This defeats the purpose of using lightweight foamed articles in the manufacture of, for example, automobiles, where lightweight components are highly desirable. Consequently, the levels of glass fibers in polymer compositions for foamed articles are kept relatively low, meaning impact resistance of the molded products is poor.

Typically, the reduced strength of structural foams may be at least partially offset by increasing the wall thickness of molded articles. Increasing wall thickness requires more raw materials per unit molded, thereby increasing the cost of production.

U.S. Patent number 5,753,717 to Sanyasi discloses a method of producing foamed plastics with enhanced physical strength. The structural foams of Sanyasi utilize CO_2 in combination with an adjustment in the extrusion temperature of molten polystyrene resins to improve foam strength. This process, however, does not improve the foam strength of other types of resins, and is not suitable for enhancing the strength of articles for use in, for example, automotive trim.

Structural foam automotive parts historically have inconsistent surface appearances due to variations in the density of the polymer near the skin or surface of these molded articles. The imperfections in the surfaces of molded structural foam articles usually limits the usage of these foam products to non-appearance (e.g., hidden or non-visible) parts or parts in which the surface has been textured. Examples of these structural automotive interior trim products include interior door panel structural members, instrument panel retainers, interior seat backs covered with fabric,

load floors in the storage compartments of vehicles, side wall trim and the like. Some pickup truck beds can be made from structural foam. All of these products require reduced density and good impact resistance.

SUMMARY OF THE INVENTION

An object of the present invention is to overcome the problems delineated hereinabove. In accordance with this object, the present invention provides a structural foam article suitable for use as automobile trim. The article (and hence the composition forming the article) comprises at least one thermoplastic; about 2% to about 15% by volume reinforcing particles having one or more layers of 0.7nm-1.2 nm thick platelets, wherein more than about 50% of the reinforcing particles are less than about 20 layers thick, and wherein more than about 99% of the reinforcing particles are less than about 30 layers thick; and there is at least one blowing agent present in a range from about 0.5% to about 10% by weight. The automotive trim component is constructed and arranged to be both lightweight and strong, exhibiting good impact resistance.

It is a further object of the present invention to provide a method which overcomes the problems delineated above. Accordingly, there is provided a method of producing structural foam articles which comprises preparing a melt of at least one thermoplastic having about 2% to about 15% by volume reinforcing particles. The reinforcing particles have one or more layers of 0.7nm-1.2nm thick platelets, wherein more than about 50% of the reinforcing particles are less than about 20 layers thick. More than about 99% of the reinforcing particles are less than about 30 layers thick. The melt comprises at least one blowing agent present in a range from about 0.5% to about 10% by weight. The polymer melt is subjected to a molding process, wherein

the molding process is a process selected from the group consisting of injection molding and extrusion molding.

This and other objects of the invention can be more fully appreciated from the following detailed description of the preferred embodiments.

DETAILED DESCRIPTION OF THE PREFERRED EMBODIMENTS

In accordance with the present invention, reinforcing nanoparticle fillers are added in levels of only a few percent by volume to polymer compositions prior to molding into the article. As a result, the impact resistance of molded articles made of, for example, polyolefins, is improved. For example, automobile splash guards and fender liners may utilize greater amounts of recycled polypropylene when combined with reinforcing nanoparticles to create strong molded parts, thereby requiring less higher cost virgin polymers and using as much as 30% less material overall due to improved strength. Use of lower cost, reinforced materials for the interior trim of an automobile is an effective way to provide impact resistant components without negatively affecting the production cost per automobile.

The automotive parts manufactured in accordance with the present invention comprise a composite material of a polymer having dispersed therein reinforcement fillers in the form of very small mineral reinforcement particles. The reinforcement filler particles, also referred to as "nanoparticles" due to the magnitude of their dimensions, each comprise one or more essentially flat platelets. Generally, each platelet has a thickness of between about 0.7-1.2 nanometers. The average platelet thickness is approximately 1 nanometer.

The preferred aspect ratio, which is the largest dimension divided by the thickness of each particle, is about 50 to about 300. At least 80% of the particles

should be within this range. If too many particles have an aspect ratio above 300, the material becomes too viscous for forming parts in an effective and efficient manner. If too many particles have an aspect ratio of smaller than 50, the particle reinforcements will not provide the desired reinforcement characteristics. More preferably, the aspect ratio for each particle is between 100-200. Most preferably at least 90% of the particles have an aspect ratio within the 100-200 range.

The platelet particles or nanoparticles are derivable from larger layered mineral particles. Any layered mineral capable of being intercalated may be employed in the present invention. Layered silicate minerals are preferred. The layered silicate minerals that may be employed include natural and artificial minerals. Non-limiting examples of more preferred minerals include montmorillonite, vermiculite, hectorite, saponite, hydrotalcites, kanemite, sodium octosilicate, magadite, and kenyaite. Mixed Mg and Al hydroxides may also be used. Various other clays can be used, such as claytone H.Y. Among the most preferred minerals is montmorillonite.

To exfoliate the larger mineral particles into their constituent layers, different methods may be employed. For example, swellable layered minerals, such as montmorillonite and saponite are known to intercalate water to expand the inter layer distance of the layered mineral, thereby facilitating exfoliation and dispersion of the layers uniformly in water. Dispersion of layers in water is aided by mixing with high shear. The mineral particles may also be exfoliated by a shearing process in which the mineral particles are impregnated with water, then frozen, and then dried. The freeze dried particles are then mixed into molten polymeric material and subjected to a high sheer mixing operation so as to peel individual platelets from multi-platelet particles and thereby reduce the particle sizes to the desired range.

The polymer composites of the present invention are prepared by combining the platelet mineral with the desired polymer in the desired ratios. The components can be blended by general techniques known to those skilled in the art. For example, the components can be blended and then melted in mixers or extruders.

Additional specific preferred methods, for the purposes of the present invention, for forming a polymer composite having dispersed therein exfoliated layered particles are disclosed in U.S. Patent Nos. 5,717,000, 5,747,560, 5,698,624, and WO 93/11190, each of which is hereby incorporated by reference. For additional background, the following are also incorporated by reference: U.S. Patent Nos. 4,739,007 and 5,652,284.

Generally, expandable plastic formulations include polystyrenes, poly(vinyl chlorides), polyethylene, polyurethanes, polyphenols and polyisocyanates. A preferred thermoplastic is used, and based on the selection of thermoplastic determines the temperature at which foaming commences, the type of blowing agent used and the cooling conditions required for dimensional stabilization of the foam. Preferably, the thermoplastic used in the present invention is a polyolefin or a homogenous or copolymer blend of polyolefins. The preferred polyolefin is at least one member selected from the group consisting of polypropylene, ethylene-propylene copolymers, thermoplastic olefins (TPOs), and thermoplastic polyolefin elastomers (TPEs). For high performance applications, engineering thermoplastics are most preferred type of thermoplastic. Such engineering thermoplastic resins may include polycarbonate (PC), acrylonitrile butadiene styrene (ABS), a PC/ABS blend, polyethylene terephthalates (PET), polybutylene terephthalates (PBT), polyphenylene oxide (PPO), or the like.

The exfoliation of layered mineral particles into constituent layers need not be complete in order to achieve the objects of the present invention. The present invention contemplates that at least 99% of the particles should be less than about 30 nanometers (30 layers or platelets) in thickness, and that more than about 50% of the particles should be less than about 20 nanometers (20 layers or platelets) in the thickness direction. Preferably, at least 90 % of the particles should have a thickness of less than 5 layers. Also, it is preferable for at least 70% of the particles should have a thickness of less than 5 nanometers. It is most preferable to have as many particles as possible to be as small as possible, ideally including only a single platelet. Particles having more than 30 layers behave as stress concentrators and should be avoided, to the extent possible.

Generally, in accordance with the present invention, each of the automotive parts that can be manufactured in accordance with the principles of the present invention should contain nanoparticle reinforcement in amounts less than 15% by volume of the total volume of the part. The balance of the part is to comprise an appropriate thermoplastic material, a blowing agent and optionally, suitable additives. If greater than 15% by volume of reinforcement filler is used, the viscosity of the composition becomes too high and thus difficult to mold. Preferably, the amount of reinforcing nanoparticles is greater than 2% by volume (as lower amounts would not achieve the desired increase in strength) and less than 15%. More preferably, the nanoparticles comprise less than 13% and greater than 3% of the total volume of the part for extrusion molding.

Preferably, relatively rigid injection molded trim parts comprise reinforcement particles of the type described herein at about 2-10% of the total volume of the part, with the balance comprising the thermoplastic substrate. It is even more preferable for

these interior panels to have reinforcement particles of the type contemplated herein comprising about 3%-8% of the total volume of the part. For some applications, inclusion of about 3%-5% reinforcing nanoparticles is optimal. Inclusion of more than 10% nanoparticles tends to increase the viscosity of the composition to point which impairs injection molding.

Blowing agents incorporated into the compositions according to the invention govern the amount of gas generated during polymer processing and molding, and thus control the density of the final product. The type of agent used determines the rate of gas production, the pressure developed during gas expansion, and the relative amount of gas lost from the system to the amount of gas retained within the cells. Blowing agents may be either physical or chemical agents; chemical agents are preferred. Chemical agents may be organic or inorganic compounds. Commonly used inorganic blowing agents include CO_2, nitrogen, helium, argon and air. Organic agents include volatile organics and halogenated hydrocarbons, such as chlorofluorocarbons, and hydrochlorofluorocarbons, although their use is diminishing due to environmental concerns. Volatile organic compounds include aliphatic hydrocarbons, such as propane, n-butane, neopentane, hexane, and the like. Preferred blowing agents are azo compounds which produce CO_2 and O_2 in the presence of heat. Preferably, at least one blowing agent is present in the polymer composition (and hence the molded article) in a range from about 0.5 % to about 10%, more preferably about 0.5% to about 4 % by weight. Combinations of more than one blowing agent may be used.

Additives or cell control agents heavily influence the nucleation of foam cells by altering surface tension of the polymer system or by serving as nucleation sites from which cells can grow. Nucleation agents are often added to polymer compositions to promoting bubble formation during processing of polypropylenes.

Nucleation agents can be selected to develop cells of a particular pore size. Suitable nucleating agents include metal aromatic carboxylates, sorbitol derivatives, inorganic compounds and organic phosphates. Examples are aluminum hydroxyl di-p-t-butyl benzoate, dibenzylidene sorbitol, magnesium silicate (talc), sodium 2,2'-methylene bis (4,6-di-t-butylpheyl) phosphate and zinc oxide. Inorganic nucleation agents are often chemically modified to improve dispersion throughout the polymer composition. The chosen nucleation agent will influence the mechanical properties of the polymer composition, and should be selected accordingly. For example, some fillers induce crystallization of polymers, which impairs impact resistance of molded articles.

The nanoparticles of the invention also advantageously behave as nucleating agents in polymer compositions. The extremely small size of these reinforcing particles permits them to be evenly dispersed throughout the polymer composition. Accordingly, the extremely small size and even distribution of the nanoparticles provides for between about 20 to about 100 times more potential nucleation sites within the polymer composition than can be achieved in an equivalent volume using larger, standard nucleation agents.

Specifically, for each 1% loading of nanoparticles by volume, there exists a minimum of at least about 10^{11} particles, and hence potential nucleation sights (one for each particle), per cubic centimeter of structural foam, where more than 50% of the reinforcement particles are less than about 20 platelets thick, and wherein the majority of reinforcement particles have a total particle size of less than about 20nm x 200nm x 300 nm. Where the majority (>50%) of particles are one platelet thick and have an approximate total particle size of about 1.2nm x 50nm x 75nm or less, the potential nucleation sites increases to at least about 10^{14} per 1% loading of reinforcement particles. Where the majority (>50%) particles are one platelet thick and have an

approximate total particle size of about 1.2nm x 200nm x 300nm or less, the potential nucleation sites is about 2 x 10^{12} per 1% loading of reinforcement particles. In the broad aspect of the invention, it is contemplated that there exists at least 10^{11} particles for each 1% loading of nanoparticles per cubic centimeter of structural foam, with the balance of the cubic centimeter being formed from the other constituent components of structural foam, such as thermoplastic material, blowing agent, and optionally, at least one additive.

When about 90% of the nanoparticles in the composition are less than 5 nm in thickness, a more preferred uniform distribution of the particles occurs in the resin, which translates into evenly distributed gas bubble formation during blow molding. A reduction to near elimination of clusters of nucleation agent can be achieved, accordingly. The advantage to nanoparticle nucleation is the near elimination of nucleation stress concentrators in concert with substantial reinforcement of foam cells, which is not possible with existing nucleation agents.

In addition to nucleating agents, other additives may optionally be included in the polymer composition to improve processability. For example, aging modifiers, such as glycerol monostearate, are useful additives in polymer compositions for molding. Aging modifiers are typically present in an amount from about 0.5% to about 5% polyolefin resin. Lubricants may also be present to enhance extrusion of the polymer composition during molding. Other additives include pigments, heat stabilizers, antioxidants, flame retardants, ultraviolet absorbing agents and the like.

Reinforced articles of the invention exhibit improved properties over non-reinforced articles. For example, polyethylene articles having 5% nanoparticles by volume, wherein 90% of the particles have 5 or fewer layers, increased flexural modulus by 2.5 to about 3 times over compositions lacking reinforcing nanoparticles,

as measured under ASTM D790 test conditions. This 5% nanoparticle polyethylene composition exhibited > 200% elongation to rupture. By contrast, about 25% glass fiber reinforcement is required in such articles to achieve an equivalent modulus. Polypropylene articles according to the invention showed about a 60% improvement in flexural modulus over articles lacking reinforcement nanoparticles. Thus, the use of reinforcing nanoparticles according to the invention provides articles having good flexural stiffness.

The specific gravity of structural foams having reinforcing nanoparticles is typically 22.5% lower than in materials lacking a blowing agent, which is 50% less dense than the blow molded foams known in the art.

It should be appreciated that the foregoing description is illustrative in nature and that the present invention includes modifications, changes, and equivalents thereof, without departure from the scope of the invention.